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FULL PAPER

Reactions of $[Mo_2(\mu\text{-}RC_2R)(CO)_4Cp_2]$ (R = CO_2Me, Cp = $\eta\text{-}C_5H_5$) with P_2Ph_4, PPh_2H and R^1SH (R^1 = Et, Pr^i, C_6H_4Me-*p* or Bu^t): stabilisation of μ-vinyl complexes by chelating substituents

Harry Adams,[a] Andreas Biebricher,[a] Sally R. Gay,[a] Trevor Hamilton,[a] Paul E. McHugh,[a] Michael J. Morris *[a] and Martin J. Mays *[b]

[a] *Department of Chemistry, University of Sheffield, Sheffield, UK S3 7HF*
[b] *University Chemical Laboratory, Cambridge, UK CB2 1EW*

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The dimolybdenum alkyne complex $[Mo_2(\mu\text{-}C_2R_2)(CO)_4Cp_2]$ **1** (R = CO_2Me; Cp = $\eta\text{-}C_5H_5$) reacts with P_2Ph_4 to afford three major products, which have been identified as the phosphido-bridged vinyl complexes *cis*- and *trans*-$[Mo_2(\mu\text{-}CR{=}CHR)(\mu\text{-}PPh_2)(CO)_2Cp_2]$ (two separable isomers, **2** and **3** respectively) and $[Mo_2(\mu\text{-}CR{=}CRCHO)(\mu\text{-}PPh_2)(CO)_2Cp_2]$ **4**. The crystal structure of **3** has been determined and shows that the CO_2Me group attached to the β-carbon of the vinyl ligand is co-ordinated to one metal atom through the carbonyl group, thus forming a five-membered chelate ring. The reaction of **1** with PPh_2H in refluxing toluene gave the same three complexes, whereas treatment of **1** with PPh_2H at room temperature in the presence of trimethylamine *N*-oxide afforded the monosubstituted complex $[Mo_2(\mu\text{-}C_2R_2)(CO)_3(PPh_2H)Cp_2]$ **6** together with a small amount of **4**; thermolysis of **6** also yields **2**, **3** and **4**. Treatment of **1** with thiols R^1SH (R^1 = Et, Pr^i or C_6H_4Me-*p*) afforded the complexes $[Mo_2(\mu\text{-}CR{=}CHR)(\mu\text{-}SR^1)(CO)_2Cp_2]$ **7a**–**7c** which are analogous to **3**; the structure of the complex with $R^1 = Pr^i$ has been determined. In contrast, treatment of **1** with Bu^tSH affords the unusual complex $[Mo_2(\mu\text{-}S)_2(\mu\text{-}RCH{=}CHR)Cp_2]$ **8** in which the alkyne ligand has been hydrogenated to an alkene which is bonded in an η^2 manner to one metal atom and through both CO_2Me groups to the other. The complexes $[Mo_2(\mu\text{-}CH{=}CHR)(\mu\text{-}SR^1)(CO)_2Cp_2]$ **10**, derived from the methyl propiolate complex $[Mo_2(\mu\text{-}HC_2R)(CO)_4Cp_2]$, are also described.

Introduction

Dinuclear complexes containing bridging phosphido ($\mu\text{-}PR_2$) or thiolato (μ-SR) ligands are of continuing interest because the presence of these ligands has been shown to help maintain the structural integrity of the dinuclear unit during further reactions.[1] We have explored in detail the influence of such ligands on the organometallic chemistry of a variety of homo- and hetero-bimetallic centres, with a particular interest in alkyne-bridged systems. Some time ago, we reported that the reaction of $[Mo_2(CO)_6Cp_2]$ with tetraphenyldiphosphane led to the bis-phosphido bridged complex $[Mo_2(\mu\text{-}PPh_2)_2(CO)_2Cp_2]$,[2] and subsequently showed that a similar reaction with the but-2-yne complex $[Mo_2(\mu\text{-}C_2Me_2)(CO)_4Cp_2]$ also produced a bis-phosphido complex, $[Mo_2(\mu\text{-}PPh_2)_2(CO)(\eta\text{-}C_2Me_2)Cp_2]$, in which the alkyne was retained as a terminal ligand.[3] In this paper we describe the reaction of P_2Ph_4 with the related alkyne complex $[Mo_2(\mu\text{-}C_2R_2)(CO)_4Cp_2]$ **1** (R = CO_2Me) which in contrast leads to a variety of products, all of which contain only one phosphido ligand and a bridging vinyl group derived from the alkyne. In keeping with their structures, these complexes are also accessible from the reaction of the alkyne complex with diphenylphosphine. We also provide full details of the structurally analogous thiolate-bridged products which are formed by the reaction of **1** with thiols, as mentioned in a preliminary account.[4]

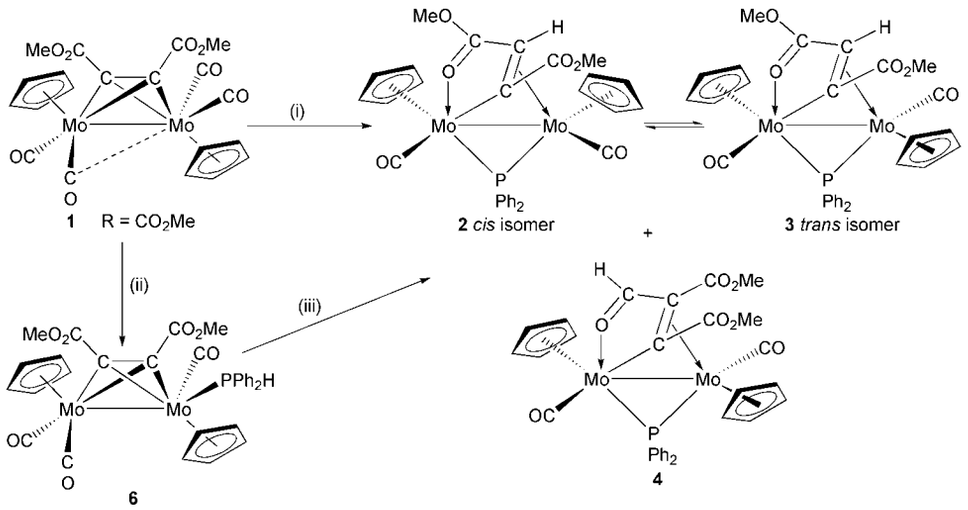
Results and discussion

Reactions with phosphines

The reaction of $[Mo_2(\mu\text{-}C_2R_2)(CO)_4Cp_2]$ **1** (R = CO_2Me) with an equimolar amount of tetraphenyldiphosphane in toluene at reflux produced three major products and several minor ones, which were separated by a combination of careful column chromatography and preparative TLC techniques. In order of elution from a column, the three major products are brown **2**, red **3**, and orange-red **4** (Scheme 1).

The red product (the highest-yielding of the three) was characterised as $[Mo_2(\mu\text{-}CR{=}CHR)(\mu\text{-}PPh_2)(CO)_2Cp_2]$ **3** on the basis of its spectroscopic data and also by crystal structure determination (see below). Its IR spectrum in KBr shows two terminal CO peaks (1900 and 1865 cm^{-1}), an ester carbonyl stretch (1659 cm^{-1}) and a peak at 1553 cm^{-1} corresponding to an ester group which is co-ordinated to molybdenum. The mass spectrum showed a molecular ion envelope at *m*/*z* 706, corresponding to the addition of PPh_2H and the loss of two carbonyl ligands. The downfield shift observed in the ^{31}P NMR spectrum (δ 145.5) is indicative of the presence of a bridging phosphido group. The organic ligand has been converted from an alkyne into a μ-vinyl (CR=CHR), as shown by the presence of a signal at δ 3.37 due to a single proton in the ^1H NMR spectrum. In addition the ^{13}C NMR shifts for the α-carbon (δ 138.5) and β-carbon (δ 36.3) are typical for such σ, π-bound vinyls, which are well known in dinuclear species.

A crystal of complex **3** suitable for X-ray diffraction was grown by diffusion of hexane into a dichloromethane solution; the molecular structure is shown in Fig. 1, with selected bond lengths and angles collected in Table 1. The molecule consists of a dimolybdenum centre [Mo(1)–Mo(2) 2.9261(5) Å] with each metal atom bearing a Cp ligand and a carbonyl group; these are arranged in a *trans* configuration. The phosphido bridge is bonded virtually symmetrically, with the Mo(1)–P(1)–Mo(2) angle of 73.83(3)° typical for such an arrangement. The remaining ligand is the μ-vinyl group, σ-bound to Mo(1) and π-bound to Mo(2). The carbonyl oxygen of the β-CO_2Me substituent is also joined to Mo(1) [O(3)–Mo(1) 2.215(2) Å], thus



Scheme 1 Reaction of complex **1** with phosphines. Reagents and conditions: (i) P_2Ph_4 (1 equivalent), toluene, reflux, 43 h; or PPh_2H (1 equivalent), toluene, reflux, 18 h; (ii) Me_3NO (3 equivalent), MeCN, r.t., PPh_2H (1 equivalent); (iii) toluene, reflux, 2.5 h.

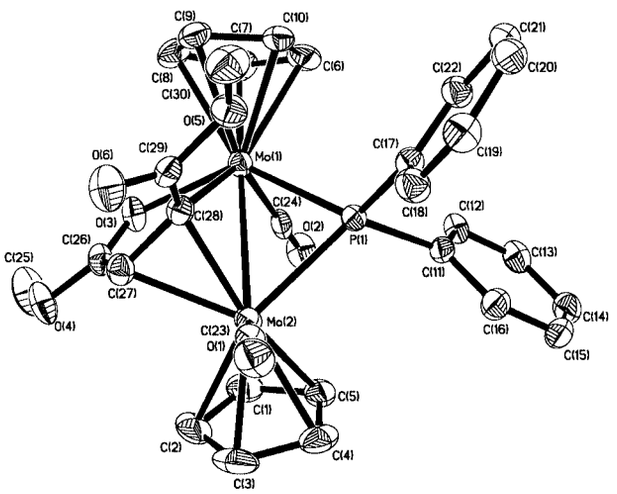


Fig. 1 Molecular structure of complex **3** in the crystal, showing the numbering scheme.

Table 1 Selected bond lengths [Å] and angles [°] for complex **3**

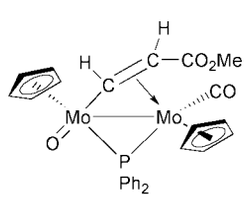
Mo(1)–C(24)	1.977(4)	Mo(1)–C(28)	2.170(4)
Mo(1)–O(3)	2.215(2)	Mo(1)–P(1)	2.4301(10)
Mo(1)–Mo(2)	2.9261(5)	Mo(2)–C(23)	1.949(4)
Mo(2)–C(28)	2.158(4)	Mo(2)–C(27)	2.252(4)
Mo(2)–P(1)	2.4416(10)	O(1)–C(23)	1.158(5)
O(2)–C(24)	1.156(4)	O(3)–C(26)	1.247(4)
O(6)–C(29)	1.220(4)	C(26)–C(27)	1.423(5)
C(27)–C(28)	1.450(5)	C(28)–C(29)	1.472(5)
C(28)–Mo(1)–O(3)	76.20(12)	C(24)–Mo(1)–P(1)	83.99(11)
C(24)–Mo(1)–O(3)	80.76(12)	C(28)–Mo(1)–P(1)	78.09(10)
C(28)–Mo(1)–Mo(2)	47.28(10)	C(24)–Mo(1)–Mo(2)	81.60(11)
P(1)–Mo(1)–Mo(2)	53.27(2)	C(28)–Mo(2)–C(27)	38.32(13)
C(23)–Mo(2)–P(1)	94.66(11)	C(28)–Mo(2)–P(1)	78.05(10)
C(27)–Mo(2)–P(1)	114.56(10)	C(23)–Mo(2)–Mo(1)	121.55(11)
C(28)–Mo(2)–Mo(1)	47.62(9)	P(1)–Mo(2)–Mo(1)	52.90(2)
Mo(1)–P(1)–Mo(2)	73.83(3)	C(26)–O(3)–Mo(1)	112.3(2)
O(1)–C(23)–Mo(2)	174.5(3)	O(2)–C(24)–Mo(1)	172.9(3)
O(3)–C(26)–C(27)	122.6(3)	C(26)–C(27)–C(28)	114.1(3)
Mo(2)–C(28)–Mo(1)	85.10(12)	C(27)–C(28)–Mo(1)	109.9(2)

forming a five-membered chelate ring. These parameters are very similar to those observed for the related complex $[Mo_2(\mu\text{-}CH{=}CHCOPh)(\mu\text{-}PPh_2)(CO)_2Cp_2]$ by Knox and co-workers, and for the analogous thiolate-bridged complex described below.[5]

The brown complex **2** is an isomer of complex **3**. Although the two are easily separated by chromatography, they are in fact in equilibrium: over a period of 2–3 days, solutions of the pure isomers re-establish an equilibrium mixture containing a ratio of approximately 8 : 1 in favour of **3** by NMR integration. The same conversion of **2** into **3** occurs more slowly in the solid state. The nature of the isomerism is uncertain, but the disposition of the Cp ligands is a strong possibility, an idea supported by the fact that whereas the Cp ligands of **3** (and **4**) appear as doublets in the ^{1}H NMR spectra due to small phosphorus couplings, those of **2** both appear as singlets. The ^{13}C NMR spectrum of **2** is very similar to that of **3**, the major difference being that the CO ligands are somewhat shifted to higher field. Only two CO peaks are observed, thus ruling out the possibility that **2** contains an additional carbonyl ligand and converts into **3** by decarbonylation and co-ordination of the β-CO_2Me of the vinyl group. Both isomers are also formed in the reaction of $[Mo_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4Cp_2]$ with RC≡CR.[6]

The orange-red product **4** was characterised as $[Mo_2(\mu\text{-}CR{=}CRCHO)(\mu\text{-}PPh_2)(CO)_2Cp_2]$. Its spectroscopic data are also very similar to those of **2** and **3**, indicating a related phosphido- and vinyl-bridged structure, but with two additional features: first in the ^{1}H NMR spectrum, the presence of a low-field singlet at δ 9.54, and secondly a peak at δ 211.5 in the ^{13}C NMR spectrum. These are due to the aldehyde functionality which is a β-substituent on the μ-vinyl group and is also co-ordinated to the metal, forming a five-membered chelate ring.

Of the minor products, two are worthy of mention. The first of these is a purple complex which we identify as $[Mo_2O(\mu\text{-}CH{=}CHR)(\mu\text{-}PPh_2)(CO)Cp_2]$ **5** by comparison with several similar complexes prepared both by us and also initially by Ziegler and co-workers,[7] which differ only in the substituents present on the vinyl ligand. The loss of a CO_2Me group during the reaction is unusual but not unprecedented; the constitution of the vinyl ligand is unambiguous from the ^{1}H NMR spectrum which displays two doublets of doublets for the vinylic protons. The stereochemistry around the vinyl ligand is difficult to assign with certainty, but probably has the two hydrogens in *cis* positions. The related complex with a μ-CH=CHEt ligand displayed almost identical shifts and couplings.[3] Complex **5** is presumably formed by the oxidation of the corresponding carbonyl complex by adventitious air; indeed a weak orange band which



5

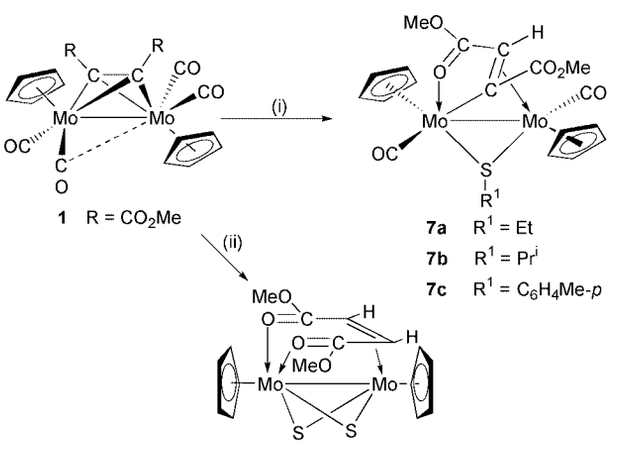
gradually converts into purple **5** during elution was observed on the chromatography column, and we suspect this may be the precursor complex. The final band eluted from the column can tentatively be identified as the related oxo complex $[Mo_2O(\mu\text{-}CR{=}CHR)(\mu\text{-}PPh_2)(CO)Cp_2]$ on the basis of the similarity of its ^1H spectroscopic data to those of **2** and **3**, and the similarity of its ^{31}P shift to that of **5**. However the small amount prepared did not allow ^{13}C NMR or analytical data to be acquired.

Since the formation of compounds **2**–**4** involves the effective addition of PPh_2 and H to the starting material, it was decided to investigate the reaction of **1** with PPh_2H itself. As expected, this produced the same products, though the yield distribution of the reaction is noticeably different; from P_2Ph_4 the major product is **3**, whereas from PPh_2H the yields of **3** and **4** are virtually identical.

Monosubstituted phosphine complexes have been prepared from alkyne complexes of type **1** by UV irradiation. Recent work by one of us, however, has shown that a carbonyl ligand can be removed from **1** by treatment with Me_3NO in acetonitrile; if carried out in the presence of additional ligands such as $P(OMe)_3$ or Bu^tNC, good yields of the appropriate monosubstituted complex can be isolated.[8] This methodology was also successful with diphenylphosphine: stirring **1** at room temperature with an excess of Me_3NO in the presence of PPh_2H afforded a 65% yield of $[Mo_2(\mu\text{-}C_2R_2)(CO)_3(PPh_2H)Cp_2]$ **6**, together with a small amount of **4**. The complex showed similar spectroscopic properties to those previously prepared; two diagnostic features are the ^{31}P chemical shift (δ 38.4), indicative of a terminal phosphine ligand rather than a phosphido bridge, and the presence of a doublet at δ 6.50 in the ^1H NMR spectrum with a characteristically large coupling of 369 Hz due to the P–H group. Thermolysis of **6** in refluxing toluene gave **2**, **3** and **4**, the last of these being the major product, in 2.5 h. Thermolysis in THF produced a similar yield of **4**, accompanied by much smaller amounts of **2** and **3**, over a period of 4 d.

Reactions with thiols

Treatment of complex **1** with an excess of the thiols R^1SH (R^1 = Et, Pr^i or *p*-C_6H_4Me) afforded the new vinyl complexes $[Mo_2(\mu\text{-}CR{=}CHR)(\mu\text{-}SR^1)(CO)_2Cp_2]$ **7a**–**7c** in good yields (Scheme 2). Of these, **7a** and **7b** exist as two isomers which



Scheme 2 Reactions of complex **1** with thiols. Reagents and condition: (i) R^1SH (5 equivalents), toluene, reflux, 21–24 h; (ii) Bu^tSH (5 equivalents), toluene, reflux, 6 h.

could not be separated by column chromatography. The nature of the isomerism is again uncertain, though by analogy with the phosphido-bridged species **2** and **3** above it is tempting to ascribe a *trans* arrangement of the Cp ligands for the major isomer and a *cis* arrangement for the minor; however the disposition of the R^1 substituent of the thiolate bridge is also a possibility, and is perhaps more likely in view of the very close similarity of the spectroscopic data for the two isomers. The isomer ratios for **7a** and **7b** are approximately 3:1 and 1.5:1 which may reflect the changing steric bulk of R^1, in accord with the fact that **7c** exists as a single isomer.

Table 2 Selected bond lengths [Å] and angles [°] for complex **7b**

Mo(1)–C(1)	1.952(4)	Mo(1)–C(13)	2.151(4)
Mo(1)–C(14)	2.226(4)	Mo(1)–S(1)	2.4331(10)
Mo(1)–Mo(2)	2.8621(5)	Mo(2)–C(2)	1.979(4)
Mo(2)–C(13)	2.157(4)	Mo(2)–O(3)	2.208(3)
Mo(2)–S(1)	2.4661(10)	S(1)–C(19)	1.839(4)
O(1)–C(1)	1.150(6)	O(2)–C(2)	1.146(6)
O(3)–C(15)	1.251(5)	O(6)–C(17)	1.214(5)
C(13)–C(14)	1.460(5)	C(14)–C(15)	1.437(5)
C(13)–Mo(1)–C(14)	38.91(13)	C(1)–Mo(1)–S(1)	94.17(13)
C(13)–Mo(1)–S(1)	82.39(10)	C(14)–Mo(1)–S(1)	119.19(10)
C(1)–Mo(1)–Mo(2)	118.68(13)	C(13)–Mo(1)–Mo(2)	48.46(10)
S(1)–Mo(1)–Mo(2)	54.79(3)	C(2)–Mo(2)–O(3)	85.02(14)
C(13)–Mo(2)–O(3)	75.99(12)	C(2)–Mo(2)–S(1)	77.37(12)
C(13)–Mo(2)–S(1)	81.48(11)	C(2)–Mo(2)–Mo(1)	79.17(12)
C(13)–Mo(2)–Mo(1)	48.27(11)	S(1)–Mo(2)–Mo(1)	53.72(2)
Mo(1)–S(1)–Mo(2)	71.49(3)	C(15)–O(3)–Mo(2)	112.5(2)
O(1)–C(1)–Mo(1)	177.7(4)	O(2)–C(2)–Mo(2)	172.5(4)
C(14)–C(13)–Mo(2)	109.6(2)	Mo(1)–C(13)–Mo(2)	83.27(14)
C(15)–C(14)–C(13)	112.6(3)	O(3)–C(15)–C(14)	122.0(3)

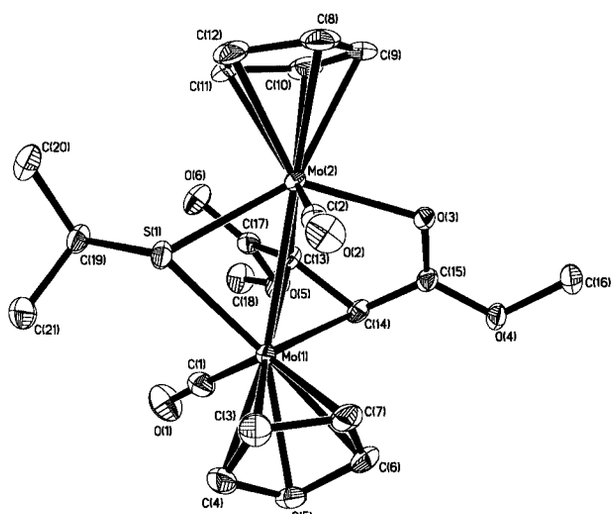


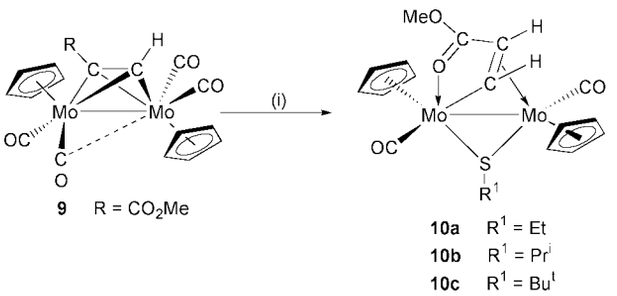
Fig. 2 Molecular structure of complex **7b** in the crystal, showing the numbering scheme.

Crystals of complex **7b** suitable for X-ray diffraction were grown by diffusion of light petroleum into a THF solution. The molecular structure is shown in Fig. 2, with selected bond lengths and angles collected in Table 2. The crystal selected contains only one isomer. The Mo–Mo bond, 2.8621(5) Å, is shorter than that in **3**, and the Mo(1)–S(1)–Mo(2) angle of 71.49(3)° in the almost symmetrically bound thiolato bridge is slightly smaller than in the phosphido group of **3**. The geometry within the chelating μ-vinyl ligand is almost identical to that in **3**. As expected, the Cp ligands (and consequently the carbonyls) occupy a *trans* arrangement.

In contrast to the reactions of complex **1** with other thiols, that with Bu^tSH occurred much more rapidly to give the unusual complex $[Mo_2(\mu\text{-}S)_2(\mu\text{-}RCH{=}CHR)Cp_2]$ **8** in 83% yield (Scheme 2). Its IR spectrum contained no carbonyl peaks, and its ^1H and ^{13}C NMR spectra were extremely simple, indicating a highly symmetrical structure, and contained no signals for Bu^t groups. The crystal structure of **8** was reported in our preliminary communication and confirmed that two bridging sulfido groups had been formed by incorporation and dealkylation of

two molecules of thiol, and that the alkyne had become hydrogenated to the *cis*-alkene dimethyl maleate.[4] This ligand is co-ordinated to one metal through the C=C bond, and to the other through the carbonyl groups of both CO_2Me substituents, thus acting as a six electron donor overall.

The reactions of the related alkyne complex $[Mo_2(\mu\text{-}HC{\equiv}CR)(CO)_4Cp_2]$ **9**, derived from methyl propiolate, with R^1SH (R^1 = Et, Pr^i or Bu^t) were also investigated, and gave rise to good or moderate yields of the vinyl complexes $[Mo(\mu\text{-}CH{=}CHR)(\mu\text{-}SR^1)(CO)_2Cp_2]$ **10a**–**10c** with structures analogous to that of **7** (Scheme 3). Only complex **10b** exists as a mixture of



9 R = CO_2Me

10a R^1 = Et
10b R^1 = Pr^i
10c R^1 = Bu^t

Scheme 3 Reactions of complex **9** with thiols. Reagents and conditions: (i) R^1SH (5 equivalents), toluene, reflux, 15–17 h.

isomers, in a ratio of 3:1. The nature of the vinyl ligand is shown clearly by the presence of two doublets (one at low field, typical of μ-CH) in the ^1H NMR spectrum of each compound; thus, the hydrogen atom migrates regiospecifically onto the more substituted end of the alkyne, which in turn relieves steric crowding at the bridging position in the resulting vinyl ligand. It is noticeable that as the steric bulk of R^1 increases the yield of **10** diminishes and the amount of the by-product $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SR^1)_2Cp_2]$ increases. No complex analogous to **8** was observed.

Possible mechanism of the reactions

In previous papers we have noted that μ-vinyl complexes of the type $[Mo_2(\mu\text{-}CR^1{=}CHR^2)(\mu\text{-}PPh_2)(CO)_3Cp_2]$ (R^1, R^2 = H, alkyl, aryl, *etc.*) cannot be isolated by insertion of alkynes into $[Mo_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4Cp_2]$, unlike the corresponding $\mu\text{-}PMe_2$ species.[3] The main products of their decomposition are oxo-complexes such as **5**; it appears that the μ-vinyl complexes are particularly susceptible to oxidation, possibly for steric reasons. A similar pattern is evident in the thiolate-bridged series. Thus, Pétillon and co-workers have described how the complexes $[Mo_2(\mu\text{-}CMe{=}CHMe)(\mu\text{-}SR^1)(CO)_3Cp_2]$ (R^1 = Me or Ph) can be isolated from the reactions of $[Mo_2(\mu\text{-}H)(\mu\text{-}SR^1)(CO)_4Cp_2]$ with but-2-yne, but are readily oxidised to the corresponding $[Mo_2O(\mu\text{-}CMe{=}CHMe)(\mu\text{-}SR^1)(CO)Cp_2]$. Other alkynes led to intractable products.[9] The exception for both classes of bridging ligand appears to be as described here, *i.e.* cases where the substituents on the vinyl ligand can co-ordinate to the metal, thus stabilising the vinyl unit by chelation. The resulting ligand is a relatively common motif in dinuclear complexes, and examples have been characterised on a wide range of metal centres.[10]

In terms of the mechanism of the thermal reaction of complex **1** with PPh_2H, we propose that the initial step is CO loss and co-ordination of PPh_2H to give **6**. Oxidative addition of the P–H bond could then be followed by the diphenylphosphido group adopting a bridging position and migration of the hydride to the alkyne to give a vinyl group, resulting ultimately in **2** and **3** after co-ordination of the carbonyl of the CO_2Me group. Migration of the hydride to the CO ligand followed by attack of the resulting formyl on the alkyne would give **4**. Complexes related to **4** were first observed by Knox and co-workers,[5] who prepared the mono-substituted alkyne complex $[Mo_2(\mu\text{-}C_2H_2)(CO)_3(PPh_3)Cp_2]$ and studied its thermolysis. On heating in toluene, this compound underwent P–C bond cleavage, followed by migration of the phenyl group to a carbonyl ligand and then migration of the resulting benzoyl group to the alkyne ligand to give $[Mo_2\{\mu\text{-}CH{=}CHC(Ph)O\}(\mu\text{-}PPh_2)(CO)_2Cp_2]$. A range of phosphines was explored and it was found that, if PPh_2H was used, P–H cleavage took precedence over P–C cleavage to give a compound analogous to **4**. In the reaction of **1** with P_2Ph_4, we propose that the CO ligand is replaced by a PPh_2 radical formed by thermal dissociation of the diphosphine. Abstraction of a hydrogen, presumably from the solvent, would afford the same products.

It is noticeable that no products are formed in which the phosphido group is coupled to the alkyne, despite the fact that attack of a nucleophilic PPh_2 on the electrophilic dimethyl acetylenedicarboxylate (dmad) is known to be possible. For example, we have previously shown that thermal reaction of **1** with PPh_2Cl leads exclusively to $[Mo_2(\mu\text{-}Cl)(\mu\text{-}PPh_2CR{=}CR)(CO)_2Cp_2]$ in which P–C bond formation has occurred.[11] We attributed this to the relative tendency of the PPh_2 and Cl to bridge the two metals in the intermediate formed by oxidative addition of the P–Cl bond. Clearly in the current reaction the phosphido group can assume the bridging role in preference to the hydride or formyl ligands, which in turn migrate to the alkyne.

In the reactions with thiols a similar mechanism is assumed for the formation of complexes **7** and **10** to that proposed for **2** and **3**. It is interesting however that no complexes analogous to **4** were formed in the reactions of **1** with thiols; migration of the hydride to a CO is evidently disfavoured in this case. The lesser degree of steric crowding in the thiolate intermediate, due to the presence of only one substituent R^1 as opposed to two phenyl rings, might account for this.

Perhaps a further indication of a less sterically crowded environment is the observation that the reactions with thiols can proceed further. In the case of $R^1 = Bu^t$, a complex is formed which clearly involves addition of two thiols, and in all of these reactions the compounds $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SR^1)_2Cp_2]$ are formed in small amounts; amounts which are, however, larger for the methyl propiolate complexes compared to the more strongly bound dmad. We have previously shown that the reaction of $[Mo_2(\mu\text{-}C_2Me_2)(CO)_4Cp_2]$, in which the alkyne is weakly bound, with thiols leads exclusively to $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SR^1)_2Cp_2]$, and indeed this forms a useful route to these compounds.[3] The results here indicate that the pathway for their formation probably proceeds by way of the sequential oxidative addition of two thiol molecules, with the transfer of their hydrogen atoms onto the alkyne ligand to create first a μ-vinyl and than an alkene. In cases such as R = Me this is then lost, and the reaction can proceed to give $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SR^1)_2Cp_2]$ by addition of two more thiols. By incorporation of the CO_2Me substituents on the alkyne, the intermediate stages in this process can be stabilised and isolated, with compounds such as **7** and **10** representing the addition of one thiol, and complex **8** the addition of two.

Experimental

General experimental techniques were as described in recent papers from these laboratories.[12,13] Infrared spectra were recorded in CH_2Cl_2 solution on a Perkin-Elmer 1600 FT-IR machine, ^1H, ^{13}C and ^{31}P NMR spectra in $CDCl_3$ solution on a Bruker AC250 machine with automated sample-changer or an AMX400 spectrometer. The $^{13}C\text{-}\{^1H\}$ NMR spectra were routinely recorded using an attached proton test technique (JMOD pulse sequence). Chemical shifts are given on the δ scale relative to $SiMe_4$ (0.0 ppm) for ^1H and ^{13}C; the $^{31}P\text{-}\{^1H\}$ NMR spectra were referenced to 85% H_3PO_4 (0.0 ppm) with downfield shifts reported as positive. Mass spectra were recorded on a Fisons/BG Prospec 3000 instrument operating in fast atom bombardment mode with *m*-nitrobenzyl alcohol as matrix. Elemental

analyses were carried out by the Microanalytical Services of the Department of Chemistry and the University Chemical Laboratory.

Trimethylamine *N*-oxide was dehydrated by azeotropic distillation in toluene. The alkyne complexes **1** and **9** were prepared by the literature procedure.[14] Light petroleum refers to the fraction boiling in the range 60–80 °C.

Thermal reaction of $[Mo_2(\mu\text{-}C_2R_2)(CO)_4Cp_2]$ 1 with P_2Ph_4

A solution of PPh_2H (0.60 cm^3, 3.52 mmol) and PPh_2Cl (0.62 cm^3, 3.45 mmol) in heptane (150 cm^3) was heated to reflux for 3 h. After cooling, the solvent was removed *in vacuo* to leave P_2Ph_4 as a snow-white powder,[15] to which was added complex **1** (2.0 g, 3.47 mmol) and toluene (175 cm^3). The resulting solution was heated to reflux for 43 h. After addition of a small amount of silica, the solvent was removed under vacuum and the residue chromatographed. The following bands were collected. (i) Green, eluted with light petroleum–dichloromethane (1:1) and consisting of $[Mo_2(\mu\text{-}PPh_2)_2(CO)_2Cp_2]$ (6.7 mg, 0.25%) identified by comparison with previous data. (ii) Orange, eluted with same solvent mixture, identity unknown (13.5 mg); readily converts into **5** and is followed by a faint purple zone presumably consisting of **5**. (iii) A large dark brown zone, eluted in CH_2Cl_2. This was subjected to further separation by preparative TLC in CH_2Cl_2, yielding 239.6 mg (9.8%) of brown solid identified as *cis*-$[Mo_2(\mu\text{-}CR{=}CHR)(\mu\text{-}PPh_2)(CO)_2Cp_2]$ **2**.

Data for **2**: IR (CH_2Cl_2) 1929m, 1893s, 1726m and 1656m cm^{-1}; ^1H NMR δ 7.85–7.01 (m, 10 H, Ph), 5.46 (s, 5 H, Cp), 4.97 (s, 5 H, Cp), 4.22 (s, 1 H, CH), 3.76, 3.16 (both s, 3 H, Me); ^{13}C NMR δ 236.5 (d, J = 20, CO), 233.9 (d, J = 15, CO), 187.0, 181.3 (both s, *C*O_2Me), 146.1 (d, J = 36, C_{ipso}), 144.4 (d, J = 29 Hz, C_{ipso}), 135.9 (s, μ-C), 134.6–126.9 (m, Ph), 93.1, 91.2 (both s, Cp), 52.7. 51.4 (both s, Me) and 41.6 (C*H*CO_2Me); ^{31}P NMR δ 155.2; MS *m*/*z* 706 and 678. It was not possible to obtain a pure sample for elemental analysis as **2** converts into its isomer **3** both in solution and in the solid state.

(iv) Purple, eluted in dichloromethane–acetone (9:1) as a mixture with the following band which was then separated by preparative TLC in CH_2Cl_2. This band is identified as $[Mo_2O(\mu\text{-}CH{=}CHCO_2Me)(\mu\text{-}PPh_2)(CO)Cp_2]$ **5** (25.6 mg, 1.2%) by its spectroscopic properties [IR (CH_2Cl_2): 1877, 1711 cm^{-1}; ^1H NMR δ 9.31 (dd, J_{HH} = 9.0, J_{PH} = 1.0, 1 H, μ-CH), 7.96–7.03 (m, 10 H, Ph), 5.46 (d, J = 0.7, 5 H, Cp), 4.97 (d, J_{HH} = 9.0, 1 H, CH), 4.59 (d, J = 1.2 Hz, 5 H, Cp) and 3.64 (s, 3 H, Me); ^{31}P NMR δ 184.5; MS *m*/*z* 636 (M^+) and 608 ($M - CO^+$)].

(v) Red, identified as *trans*-$[Mo_2(\mu\text{-}CR{=}CHR)(\mu\text{-}PPh_2)(CO)_2Cp_2]$ **3**. After TLC separation from the previous band, the yield was 697.5 mg (28.5%). Mp 262 °C. IR: (CH_2Cl_2): 1878s and 1655m; (KBr) 1900, 1865, 1659 and 1553 cm^{-1}; ^1H NMR δ 7.48–7.05 (m, 10 H, Ph), 5.31 (d, J = 1.5, 5 H, Cp), 4.73 (d, J = 1.1 Hz, 5 H, Cp), 3.46 (s, 3 H, Me), 3.37 (s, 1 H, CH) and 3.05 (s, 3 H, Me); ^{13}C NMR δ 257.8 (d, J = 12, CO), 245.0 (d, J = 9, CO), 194.4, 180.9 (both s, *C*O_2Me), 145.5 (d, J = 33, C_{ipso}), 145.2 (d, J = 25, C_{ipso}), 138.5 (d, J = 26 Hz, μ-C), 133.6–127.2 (m, Ph), 92.9, 91.6 (both s, Cp), 53.2, 50.4 (both s, Me), 36.3 (s, C*H*CO_2Me); ^{31}P NMR δ 145.5 (Found: C, 50.96; H, 4.06; P, 4.19. Calc. for $C_{30}H_{27}Mo_2O_6P$: C, 50.99; H, 3.82; P, 4.39%). MS *m*/*z* 706 (M^+) and 678 ($M - CO^+$).

(vi) Red, eluted in dichloromethane–acetone (4:1) and further purified by preparative TLC in a 9:1 mixture of the same solvents to remove a small amount of a brown impurity. This yielded an orange powder of complex $[Mo_2(\mu\text{-}CR{=}CR\text{-}CHO)(\mu\text{-}PPh_2)(CO)_2Cp_2]$ **4** (207.5 mg, 8.1%). Mp 149–150 °C. IR (CH_2Cl_2): 1928m, 1896s and 1677m cm^{-1}; ^1H NMR δ 9.54 (s, 1 H, CH), 7.59–7.04 (m, 10 H, Ph), 5.34 (d, J = 1.6, 5 H, Cp), 4.87 (d, J = 1.1 Hz, 5 H, Cp), 3.62 (s, 3 H, Me) and 3.07 (s, 3 H, Me); ^{13}C NMR δ 257.2 (d, J = 12, CO), 238.5 (d, J = 9, CO), 211.5 (s, CHO), 179.2, 170.8 (both s, *C*O_2Me), 151.3 (d, J = 27, μ-C), 145.3 (d, J = 35, C_{ipso}), 144.6 (d, J = 28 Hz, C_{ipso}), 133.6–127.3 (m, Ph), 93.9, 92.2 (both s, Cp), 61.1 (s, *C*CO_2Me), 50.9, 50.2 (both s, Me); ^{31}P NMR δ 138.9 (Found: C, 50.60; H, 3.66; P, 4.09. Calc. for $C_{31}H_{27}Mo_2O_7P$: C, 50.68; H, 3.68; P, 4.22%). MS *m*/*z* 706 ($M - CO^+$) and 650.

(vii) A small amount of a further red complex was eluted with methanol and tentatively identified as $[Mo_2O(\mu\text{-}CR{=}CHR)(\mu\text{-}PPh_2)(CO)Cp_2]$. IR ($CH_2Cl_2$): 1917s, 1722m and 1676m cm^{-1}. ^1H NMR δ 7.92–6.78 (m, 10 H, Ph), 5.76 (d, J = 0.5, 5 H, Cp), 5.04 (d, J = 1.1, 5 H, Cp), 4.65 (d, J = 2.4 Hz, 1 H), 3.71, 3.47 (both s, 3 H, Me). ^{31}P NMR δ 190.1; MS: *m*/*z* 694 and 668.

Thermal reaction of complex 1 with PPh_2H

A solution of complex **1** (1.0 g, 1.74 mmol) in toluene (175 cm^3) was treated with diphenylphosphine (0.3 cm^3, 1.73 mmol) and heated to reflux for 18 h. The solvent was removed and the residue subjected to column chromatography as above. The major products were: brown **2** (152.4 mg, 12.4%), eluted in CH_2Cl_2; red **3** (393.5 mg, 32.1%), eluted in CH_2Cl_2; an unidentified green band (41.2 mg) eluted in CH_2Cl_2–acetone (24:1); an unidentified purple zone (75.9 mg), eluted in CH_2Cl_2–acetone (9:1); and orange-red **4** (410.0 mg, 32.2%), eluted in a 4:1 mixture of the same solvents.

Synthesis of $[Mo_2(\mu\text{-}C_2R_2)(CO)_3(PPh_2H)Cp_2]$ 6

Complex **1** (412.9 mg, 0.72 mmol) was dissolved in dry acetonitrile (40 cm^3) and treated with solid anhydrous Me_3NO (178.2 mg, 2.38 mmol) followed by PPh_2H (0.25 cm^3, 1.47 mmol). The solution was stirred at room temperature for 18 h, at which point spot TLC monitoring showed the presence of a single red zone. After addition of silica (5 g) the solvent was removed *in vacuo* at room temperature and the residue loaded onto a chromatography column. Removal of several minor bands was achieved by gradually changing the eluting solvent from light petroleum to dichloromethane. Elution with dichloromethane–acetone (19:1) produced a red band of complex **6** (339.0 mg, 64.4%). Continued elution with a 17:3 mixture of the same solvents gave an orange band of complex **4** (46.5 mg, 8.8%).

Data for **6**: IR (CH_2Cl_2) 1931s, 1814m and 1682m cm^{-1}; ^1H NMR δ 7.73–7.30 (m, 10 H, Ph), 6.50 (d, J = 369 Hz, 1 H, PH), 5.05 (s, 5 H, Cp), 4.93 (s, 5 H, Cp), 3.64 (s, 3 H, Me) and 3.56 (s, 3 H, Me); ^{13}C NMR δ 238.2 (s, CO), 235.6 (d, J = 13, CO), 230.5 (s, CO), 178.2, 175.8 (both s, *C*O_2Me), 134.3 (d, J = 39, C_{ipso}), 134.0 (d, J = 34 Hz, C_{ipso}), 132.5–127.7 (m, Ph), 92.8, 91.7 (both s, Cp), 52.2, 51.7 (both s, Me); ^{31}P NMR δ 38.4 (Found: C, 50.38; H, 3.52. Calc. for $C_{31}H_{27}Mo_2O_7P$: C, 50.68; H, 3.68%); MS *m*/*z* 735 ($M + H^+$), 703, 679, 651 and 623.

Thermolysis of complex 6

A solution of complex **6** (162.8 mg, 0.22 mmol) in toluene (30 cm^3) was heated to reflux for 2.5 h. Column chromatography gave **2** and **3** (combined yield 39.9 mg, 25.5%) followed by **4** (56.0 mg, 34.4%). A similar reaction in refluxing THF for 4 d gave the same products in yields of 4 and 36% respectively.

Reactions of complex 1 with thiols R^1SH (R^1 = Et, Pr^i or C_6H_4Me-*p*)

(a) R^1 = Et. A solution of complex **1** (1.00 g, 1.74 mmol) in toluene (125 cm^3) was treated with five equivalents of EtSH (0.65 cm^3, 8.7 mmol) and heated to reflux for 21 h, the progress of the reaction being monitored by spot TLC. The solvent was removed, the residue absorbed onto a small amount of silica, and then loaded onto a chromatography column. Elution with light petroleum–CH_2Cl_2 (1:1) afforded a purple band and a pink band due to small amounts of the two isomers of $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SEt)_2Cp_2]$ (combined yield 140 mg, 16%). Further

elution with CH_2Cl_2 and acetone (19:1) produced a red band of $[Mo_2(\mu\text{-}CR{=}CHR)(\mu\text{-}SEt)(CO)_2Cp_2]$ **7a** (750 mg, 74%). Mp 227–229 °C. IR (CH_2Cl_2): 1905 (sh), 1877 and 1667 cm^{-1}. ^1H NMR (values for minor isomer given in square brackets where visible): δ 5.28 [5.24], 5.04 [5.02] (both s, 5 H, Cp), 3.39 [3.38] (s, 1 H, CH), 3.36 [3.35], 3.16 [3.14] (both s, 3 H, CO_2Me), 2.68 (dq, 1 H of CH_2), 2.20 (dq, 1 H of CH_2) and 1.04 [0.94] (t, 3 H, Me); ^{13}C NMR δ 262.2 [264.0], 242.9 [242.8] (both s, CO), 193.3 [192.8], 182.2 [181.5] (both s, *C*O_2Me), 145.3 [145.3] (s, μ-C), 94.0 [93.3], 92.5 [91.8] (both s, Cp), 53.5 [53.3], 51.0 [51.0] (both s, CO_2*Me*), 39.1 [35.8] (s, CHR), 33.0 [29.7] (s, CH_2) and 17.7 [17.8] (s, Me) (Found: C, 41.37; H, 3.72; S, 5.81. Calc. for $C_{20}H_{22}Mo_2O_6S$: C, 41.25; H, 3.81; S, 5.51%). MS *m*/*z* 583 (M^+).

(b) $R^1 = Pr^i$. In a similar manner, reaction of complex **1** (1.0 g, 1.74 mmol) with Pr^iSH (5 equivalents, 0.80 cm^3, 8.7 mmol) for 24 h afforded a small amount of $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SPr^i)_2Cp_2]$ (60 mg, 6%) and a small red band of unidentified material, followed by red $[Mo_2(\mu\text{-}CR{=}CHR)(\mu\text{-}SPr^i)(CO)_2Cp_2]$ **7b** (690 mg, 67%), which was eluted from the chromatography column with CH_2Cl_2. Mp 206–208 °C. IR (CH_2Cl_2): 1910 (sh), 1884 and 1668 cm^{-1}. ^1H NMR (values for minor isomer given in square brackets where visible): δ 5.45 [5.29], 5.10 [5.06] (both s, 5 H, Cp), 3.75 [3.71] (s, 3 H, CO_2Me), 3.54 [3.88] (s, 1 H, CHR), 3.42 [3.43] (s, 3 H, CO_2Me), 3.18 [2.59] (m, 1 H, CH*Me*$_2$), 1.20 [1.02] and 0.85 [0.94] (both d, J = 7 Hz, 3 H, Me); ^{13}C NMR δ 262.1 [263.9], 244.1 [243.1] (both s, CO), 193.2 [192.7], 182.0 [180.3] (both s, *C*O_2Me), 145.7 [140.2] (s, μ-C), 94.1 [93.3], 92.7 [91.7] (both s, Cp), 53.5 [53.3], 51.0 [51.0] (both s, CO_2*Me*), 40.5 [44.5] (s, CHR), 38.1 [36.4] (s, CH), 27.6 [27.1] and 25.4 [25.4] (both s, Me) (Found: C, 39.13; H, 3.83; S, 4.76. Calc. for $C_{21}H_{24}Mo_2O_6S{\cdot}CH_2Cl_2$: C, 38.76; H, 3.82; S, 4.70%). MS: *m*/*z* 598 ($M + H^+$).

(c) $R^1 = C_6H_4Me$-*p*. In an analogous manner, complex **1** (1.16 g, 2.01 mmol) reacted with toluene-*p*-thiol (1.25 g, 10 mmol) in refluxing toluene over 24 h to give, on column chromatography, several minor bands, followed by the dark red major product, $[Mo_2(\mu\text{-}CR{=}CHR)(\mu\text{-}SC_6H_4Me\text{-}p)(CO)_2Cp_2]$ **7c** (640 mg, 50%), which was eluted with CH_2Cl_2. Mp 209–211 °C. IR (CH_2Cl_2): 1910 (sh), 1884 and 1734 cm^{-1}; ^1H NMR δ 6.82 (s, 4 H, C_6H_4), 5.38, 4.65 (both s, 5 H, Cp), 3.70 (s, 3 H, CO_2Me), 3.53 (s, 1 H, CH), 3.34 (s, 3 H, CO_2Me) and 2.18 (s, 3 H, Me); ^{13}C NMR δ 261.7, 244.1 (both s, CO), 193.0, 180.8 (both s, *C*O_2Me), 141.1 (s, μ-C), 139.4–128.3 (m, C_6H_4), 94.0, 93.5 (both s, Cp), 53.4, 51.2 (both s, CO_2*Me*), 36.3 (s, CHR) and 20.8 (s, Me) (Found: C, 46.43; H, 3.60; S, 4.98. Calc. for $C_{25}H_{24}Mo_2O_6S$: C, 46.58; H, 3.75; S, 4.97%). MS: *m*/*z* 647 ($M + H^+$).

Reaction of complex 1 with Bu^tSH

A solution of complex **1** (1.0 g, 1.74 mmol) in toluene (125 cm^3) was treated with Bu^tSH (1.0 cm^3, 8.8 mmol) and heated to reflux. After 2 h the solution had turned brown and spot TLC showed almost complete reaction; reflux was continued for 4 h. The solvent was removed and the residue chromatographed. A weak pink-purple band due to one isomer of $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SBu^t)_2Cp_2]$ was obtained by elution with light petroleum and CH_2Cl_2 (1:1). Careful elution with CH_2Cl_2 separated the second isomer of this compound as a small red-purple band, followed closely by a large brown band of $[Mo_2(\mu\text{-}S)_2(\mu\text{-}RCH{=}CHR)Cp_2]$ **8** (770 mg, 83%) which was then eluted with CH_2Cl_2 and acetone (19:1). Mp 197–199 °C. IR(CH_2Cl_2): 1552 cm^{-1}. ^1H NMR: δ 6.04, 6.00 (both s, 5 H, Cp), 3.44 (s, 6 H, Me) and 3.29 (s, 2 H, CH); ^{13}C NMR δ 174.7 (s, *C*O_2Me), 99.3, 97.2 (both s, Cp), 52.1 (s, CO_2*Me*) and 38.2 (CH) (Found: C, 37.08; H, 3.79; S, 11.39. Calc. for $C_8H_9MoO_2S$: C, 36.24; H, 3.42; S, 12.09%). MS: *m*/*z* 530 (M^+).

Reactions of $[Mo_2(\mu\text{-}HC_2R)(CO)_4Cp_2]$ 9 with thiols R^1SH (R^1 = Et, Pr^i or Bu^t)

(a) R^1 = Et. A solution of complex **9** (0.70 g, 1.21 mmol) in toluene (125 cm^3) was treated with EtSH (0.5 cm^3, 6.05 mmol) and heated to reflux for 15 h. The solvent was removed and the residue absorbed on a small amount of silica. Column chromatography, eluting with light petroleum–CH_2Cl_2 (7:3) afforded an orange band from which $[Mo_2(\mu\text{-}CH{=}CHR)(\mu\text{-}SEt)(CO)_2Cp_2]$ **10a** (400 mg, 63%) was obtained. Further elution with a 1:1 mixture of the same solvents gave two weak purple bands which were identified as the two isomers of $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SEt)_2Cp_2]$ (combined yield 110 mg, 18%). Data for **10a**: mp 221–224 °C; IR(CH_2Cl_2) 1867 (sh) and 1859 cm^{-1}; ^1H NMR δ 7.51 (d, J = 4 Hz, 1 H, μ-CH), 5.28, 5.09 (both s, 5 H, Cp), 3.42 (s, 3 H, CO_2Me), 3.19 (d, J = 4, 1 H, CH), 2.26 (dq, J = 13 and 6.5, 1 H of CH_2), 2.01 (dq, J = 13 and 6.5, 1 H of CH_2) and 1.17 (t, J = 6.5 Hz, Me); ^{13}C NMR δ 263.2, 248.3 (both s, CO), 192.4 (s, *C*O_2Me), 146.0 (s, μ-C), 92.4, 92.3 (both s, Cp), 53.1 (s, CO_2*Me*), 35.4 (s, CHR), 35.2 (s, CH_2) and 17.5 (s, Me) (Found: C, 41.16; H, 3.68; S, 6.30. Calc. for $C_{18}H_{19}Mo_2O_4S$: C, 41.24; H, 3.85; S, 6.12%); MS *m*/*z* 525 (M^+).

(b) R = Pr^i. In a similar manner, complex **9** (0.70 g, 1.21 mmol) reacted with Pr^iSH (0.6 cm^3, 6.0 mmol) in refluxing toluene over 16 h to give 240 mg (37%) of orange-red $[Mo_2(\mu\text{-}CH{=}CHR)(\mu\text{-}SPr^i)(CO)_2Cp_2]$ **10b**, and 190 mg (29%) of the combined isomers of purple $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SPr^i)_2Cp_2]$, separated as above. Data for **10b**: mp 170–172 °C; IR(CH_2Cl_2) 1890 (sh) and 1859 cm^{-1}; ^1H NMR (values for minor isomer given in square brackets where visible) δ 7.61 [6.99] (d, J = 4, 1 H, μ-CH), 5.37 [5.27], 5.09 [5.07] (both s, 5 H, Cp), 3.40 [3.41] (s, 3 H, CO_2Me), 3.19 [3.30] (d, J = 4 Hz, CHR), 2.37 (m, C*H*Me_2), 0.99 [0.94], 0.94 [0.86] (both d, J = 7 Hz, Me); ^{13}C NMR δ 263.4, 249.5 (both s, CO), 192.5 (*C*O_2Me), 146.6 [141.4] (μ-C), 92.8 [92.4], 92.7 [91.8] (both s, Cp), 53.2 [53.1] (s, CO_2*Me*), 42.3 [43.8] (s, CH), 27.7 [27.0], 25.4 [25.6] (both s, Me) (Found: C, 42.34; H, 4.17; S, 5.81. Calc. for $C_{19}H_{21}Mo_2O_4S$: C, 42.39; H, 4.12; S, 4.96%); MS *m*/*z* 538 (M^+).

(c) R = Bu^t. In a similar manner, complex **9** (0.5866 g, 1.13 mmol) reacted with Bu^tSH (0.65 cm^3, 5.6 mmol) in refluxing toluene over 17 h to give 211.4 mg (34%) of orange-red $[Mo_2(\mu\text{-}CH{=}CHR)(\mu\text{-}SBu^t)(CO)_2Cp_2]$ **10c**, followed by the two isomers of purple $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SBu^t)_2Cp_2]$ (117.9 mg, 18.5%), eluted with CH_2Cl_2–light petroleum (1:1) and CH_2Cl_2 respectively. Data for **10c**: mp 173–176 °C; IR(CH_2Cl_2) 1885 (sh) and 1858 cm^{-1}; ^1H NMR δ 7.83 (d, J = 4, 1 H, μ-CH), 5.42, 5.09 (both s, 5 H, Cp), 3.40 (s, 3 H, CO_2Me), 3.09 (d, J = 4 Hz, 1 H, CH) and 1.13 (s, 9 H, Me); ^{13}C NMR δ 263.3, 250.8 (both s, CO), 192.5 (s, *C*O_2Me), 147.4 (s, μ-C), 93.0, 92.4 (s, Cp), 53.2 (s, CO_2*Me*), 48.0 (*C*Me_3) and 32.2 (s, C*Me*$_3$) (Found: C, 43.86; H, 4.46; S, 6.00. Calc. for $C_{20}H_{23}Mo_2O_4S$: C, 43.49; H, 4.38; S, 5.80%). MS: *m*/*z* 552 (M^+).

Crystal structure determinations of complexes 3 and 7b

Crystal data for the two complexes are in Table 3. Data collected were measured on a Bruker Smart CCD area detector with an Oxford Cryosystems low temperature system. Cell parameters were refined from the setting angles of 160 (θ range 2.29–28.29°) for **3** or 969 reflections (θ 1.96 to 28.32°) for **7b**. Reflections were measured from a hemisphere of data collected of frames each covering 0.3° in ω. Of the reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by semiempirical methods based on symmetry-equivalent and repeated reflections, those independent reflections which exceeded the significance level $|F|/\sigma(|F|) > 4.0$ were used in refinement. The structures were solved by direct methods and refined by full matrix least squares methods on F^2. Hydrogen atoms were placed geometrically

Table 3 Summary of crystallographic data for complexes **3** and **7b**

	3	**7b**
Empirical formula	$C_{30}H_{27}Mo_2O_6P$	$C_{21}H_{24}Mo_2O_6S$
Formula weight	706.37	596.34
T/K	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	9.3859(7)	9.9710(6)
b/Å	17.7550(14)	15.3616(9)
c/Å	16.2444(13)	14.0659(9)
β/°	93.291(2)	92.4760(10)
V/Å^3	2702.6(4)	2152.5(2)
Z	4	4
μ/mm^{-1}	1.031	1.298
Reflections collected	17492	13023
Independent reflections	6317 [R(int) = 0.0662]	5053 [R(int) = 0.1183]
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0460, 0.1013	0.0487, 0.1181
(all data)	0.0650, 0.1081	0.0589, 0.1266

and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. Refinement converged at the final R values shown with allowance for the thermal anisotropy of all non-hydrogen atoms. Weighting schemes $w = 1/[\sigma^2(F_o^2) + (0.0633P)^2 + 0.00P]$ (for **3**) and $1/[\sigma^2(F_o^2) + (0.1102\ P)^2 + 25.74\ P]$ (for **7b**) where $P = (F_o^2 + 2\ F_c^2)/3$ were used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL[16] as implemented on the Viglen pentium computer.

CCDC reference number 186/2094.

See http://www.rsc.org/suppdata/dt/b0/b004210m/ for crystallographic files in .cif format.

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